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*Transient Techniques for Determining the Thermal
Conductivity of Homogeneous Polymeric
Materials at Elevated Temperatures*

Robert G. Nagler

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CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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National Aeronautics & Space Administration

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PREFACE

This Report presents one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

ABSTRACT15789 *In this*

Linear thermal conductivity relations at temperatures above room temperature were found from transient temperature-time data for polyethylene, polytetrafluoroethylene, and polymethylmethacrylate. The relations agree well with literature data for the same temperature ranges, but the computer time and cost of obtaining data points are significantly greater when compared to other measuring techniques of equivalent accuracy.

*Author***I. INTRODUCTION**

Thermal conductivity measurements have become very important due to the exotic heat insulation requirements of modern engineering. With the introduction of ablative materials for high temperature insulation, the assumption of constant thermal properties so prevalent in the literature no longer holds. Therefore, in considering polymeric materials or composites containing polymers, new techniques are needed to measure thermal conductivities which may increase or decrease by an order of magnitude from room temperature to their melt, sublimation, or degradation temperatures. It would also be of interest to develop a method which is applicable to charred re-

gions of plastics and to regions in which some phase transition has caused a partial melt layer or a gross volume expansion.

This report outlines some of the preliminary investigation on one approach to the above problem. This work has been carried out in the Materials Research Section of the Jet Propulsion Laboratory (JPL) as part of a broader program involving an investigation of the effects of vacuum, high temperature, and a variety of heat inputs on the thermal stability of homogeneous polymeric materials.

II. EXPERIMENTAL AND ANALYTICAL PROCEDURES

A general form of the heat conduction equation for nonconstant thermal properties may be written as

$$\rho C_p \frac{\partial v}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial v}{\partial x} \right) + \frac{A k}{x} \frac{\partial v}{\partial x} \quad (1)$$

where v is the relative temperature, $T - T_0$, A is 0 for a one-dimensional flat plate system, 1 for a cylindrical system, and 2 for a spherical system. Density (ρ), specific heat at constant pressure (C_p), and thermal conductivity (k) are assumed to be functions of distance (x), time (t), and relative temperature (v). Only the flat plate system has been studied in this investigation. Therefore, Eq. (1) may be reduced to

$$\rho C_p \frac{\partial v}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial v}{\partial x} \right) \quad (2)$$

As a first approximation over the temperature ranges considered in this study, density may be considered constant, and specific heat and thermal conductivity may be assumed to be linear functions of temperature. Thus,

$$\rho_0 C_p = \rho_0 C_{p_0} + av$$

$$k = k_0 + bv$$

where the zero subscripted values are the values at the initial temperature, T_0 , and a and b are the assumed linear slopes of the density-specific heat curve and the thermal conductivity curve over the ranges of interest. Substitution of these values into Eq. (2) yields

$$(\rho_0 C_{p_0} + av) \frac{\partial v}{\partial t} = \frac{\partial}{\partial x} \left[(k_0 + bv) \frac{\partial v}{\partial x} \right] \quad (3)$$

Equation (3), with suitable boundary conditions, may be solved with available computer techniques. It remains to choose experimental models which accurately simulate boundary conditions suitable for computer solution.

Three experimental models have been chosen which appear to give the best potential for realistic control of boundary conditions. The three models and the boundary conditions which they satisfy are shown in Figs. 1, 2, and 3. Each of the models uses copper-specimen interfaces for boundary control. The copper is treated as a super-conductor (compared with the thermal conductivity of

the specimen) so that the entire copper-specimen interface is assumed to be at a constant temperature at any

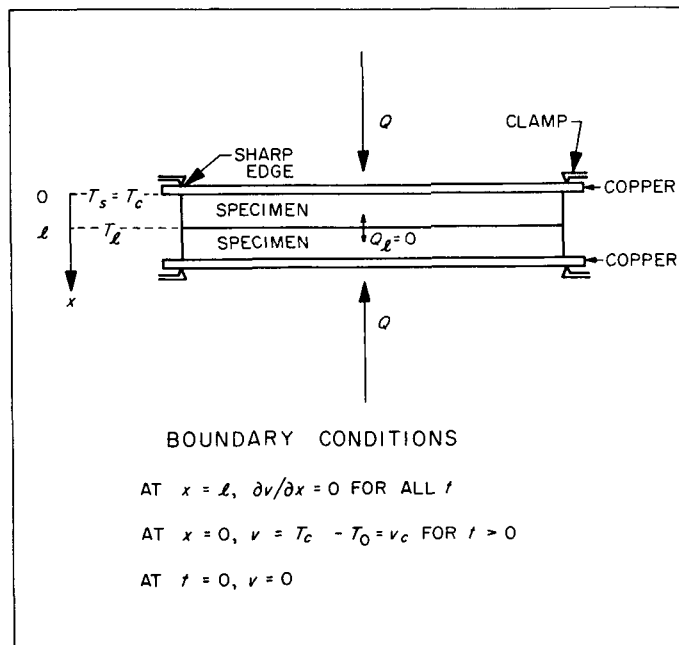


Fig. 1. Model I

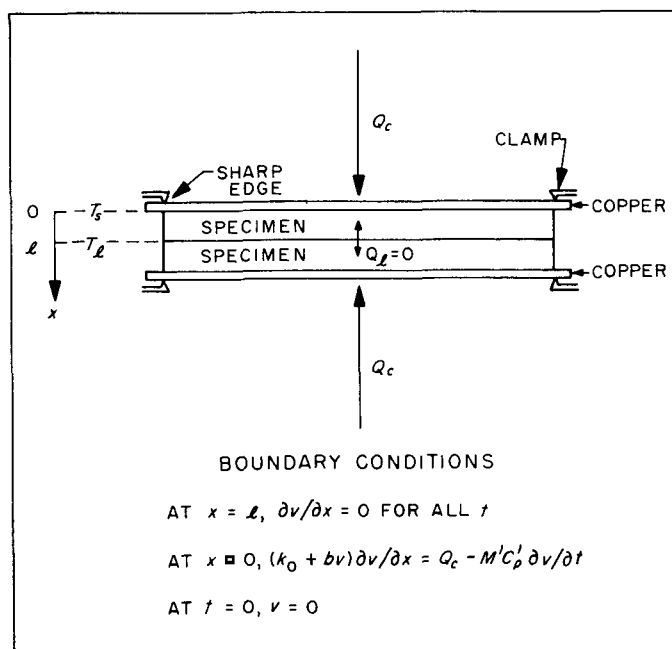


Fig. 2. Model II

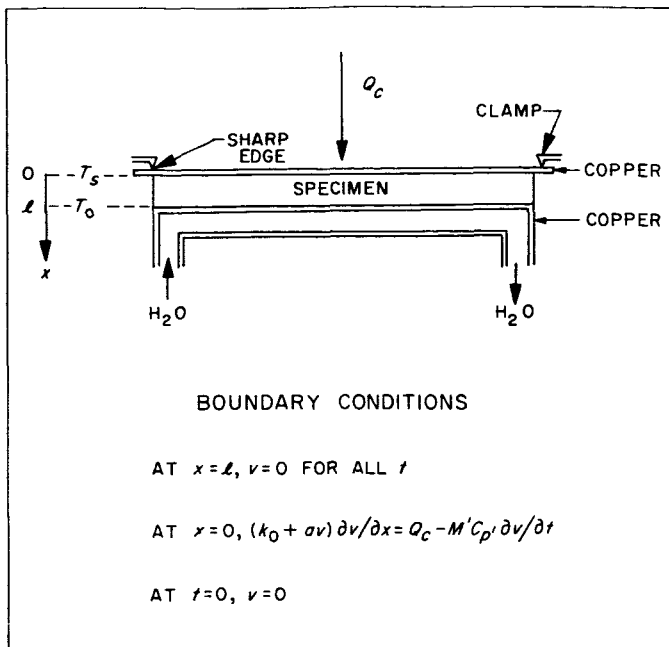


Fig. 3. Model III

specific time. The specific heat of the copper at constant pressure is designated as C'_p , and its area density as M' . All specimens have a minimum length-to-thickness ratio of 12. This ratio is felt to be sufficiently large to eliminate lateral heat flow effects on temperature measurements near the center axis of the specimen.

Models I and II consist of two identical specimens pressed between two identical thin copper plates with a sharp edged clamp. In Model I, the temperature, T_s , of the outer surface of each specimen is held constant with time. In Model II, the heat flux to the outer surface of each copper plate is held constant with time. In both models, the constant conditions are identical on opposing sides of the twin specimens, so that the center interface may be considered an insulating or zero heat flux surface. Temperatures are measured on the center axis of the model between the two specimens and at both copper-specimen interfaces.

Model III consists of only one specimen with the hot surface identical to that for Model II. The back surface is held at the initial temperature by water cooling. Temperatures are measured at both copper-specimen interfaces.

The potentially significant errors in the three models are: (1) lateral heat flow from the clamps, (2) poor contact resistance at the interfaces, and (3) the disruption of the

interfaces by the placement of the thermocouple wires. The lateral heat flow problem was minimized by using very sharp clamping edges and blackening the areas of the clamp adjacent to the specimen. Blackening the clamp decreases the lateral heat flow by decreasing the temperature differential between the clamp and the copper plate. Because of the plastic nature of the polymeric specimens, a slight clamping pressure causes cold flow at the interface and the interface resistance on the flat, polished copper surface may be considered negligible.

Placement of the thermocouple wires was a much more difficult problem. In Models I and II, a clean 1- or 3-mil pair of thermocouple wires were layed between the two specimens without significantly disrupting the zero heat flow condition at the boundary. On the copper-specimen interfaces, thermocouples placed in this manner ruined the interface contact, shorted to the copper plates (through sprayed insulating coatings), and generally prevented the repeatability and reliability of results, regardless of the precautions taken. This problem was lessened by calibrating each copper plate used in the facility for differences in the center and edge temperatures at various constant conditions and for a number of heating rates. Chromel-alumel thermocouples were spot welded to the copper plate at four spaced locations (see inset, Fig. 4). The thermocouple leads were brought out through the specimen separately so that the hot interface would not be disrupted. Runs at constant edge temperatures

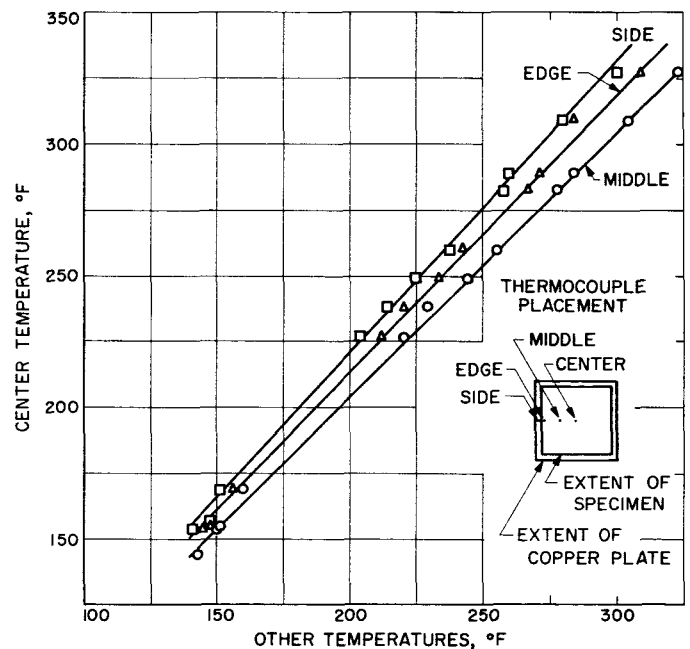


Fig. 4. Face plate calibration for radiant heater facility

are plotted in Fig. 4. Temperature data from constant heat flux runs fell within 2% of the least-squares calibration curves drawn through the points. Within the experimental accuracy of the method, these curves were found to be accurate for all of the materials used in this study.

The specimen holder for Models I and II is shown in Fig. 5, and that for Model III in Fig. 6. The holder is centered in a mirror-finished aluminum box between identical banks of tungsten filament bulbs (Fig. 7). This radiant heater may then be closed and operated on either or both banks of bulbs. Figure 8 shows the experimental system. To the left of the radiant heater is the ignitron power source, the temperature sensing power controller, and the recording oscillograph used in recording the temperature measurements. To the right of the heater is the ice bath and thermocouple calibration system. Thermocouples must be calibrated before and after each run.

For the Model I system, the desired temperature for the copper-specimen interface is preset on the power controller. The system is then operated and the temperatures on the back and front surfaces are recorded for about two minutes. Accuracy in setting the controller is not im-

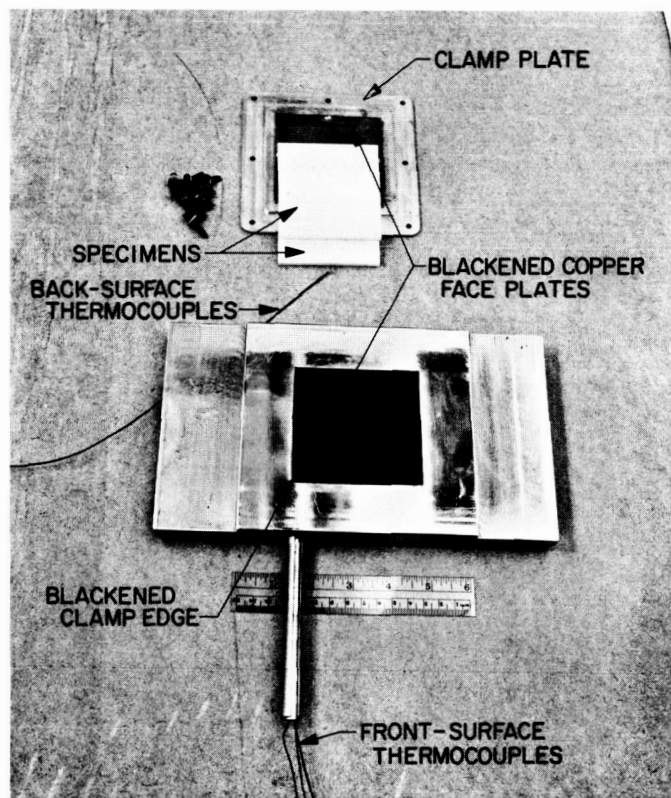


Fig. 5. Specimen holder assembly for Models I and II

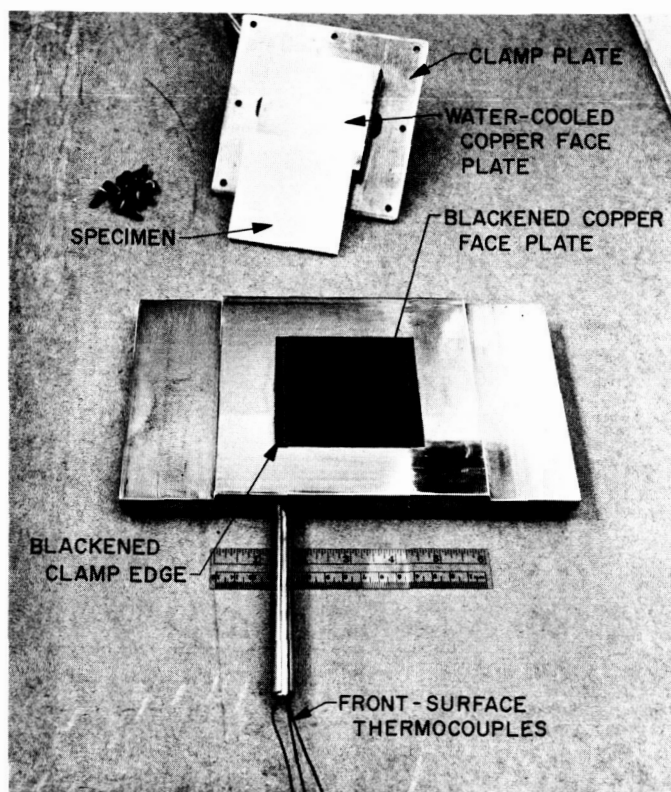


Fig. 6. Specimen holder assembly for Model III

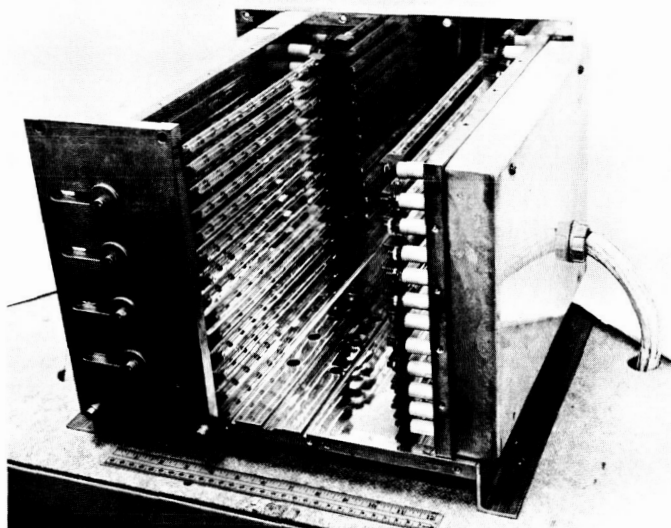


Fig. 7. Internal view of radiant heater

portant since two thermocouples are used on each copper plate, one for control purposes and one to read what the temperature actually is. For Models II and III, the power controller is bypassed and the ignitron power supply is

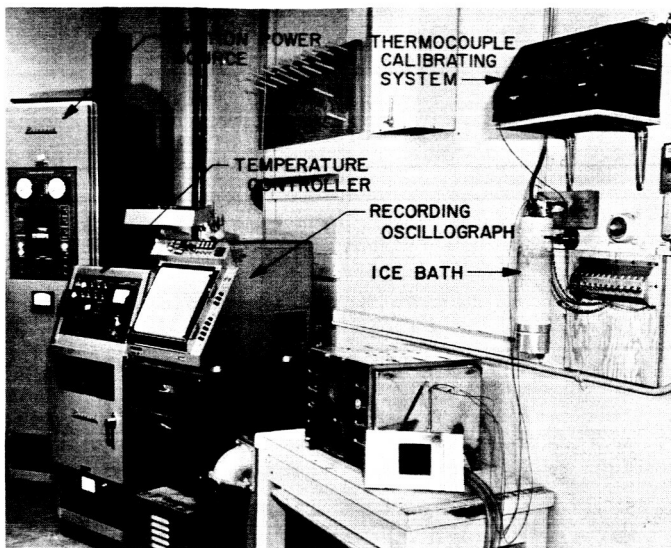


Fig. 8. Experimental system

set at a constant power level. The equivalent heat input to the copper plates is found with a copper disk calorimeter. The calorimeter consists of nine half-inch copper disks, layed out in an X, and inserted in a transite surface. The disks touch the transite at only three small places on their edges and their temperatures are measured with 3-mil chromel-alumel thermocouples spot welded to the center of the back surface of each copper disk. Short time temperature rises in the copper disks were combined with exact weights, dimensions, and specific heats to determine the heat input to each blackened copper face. The lampblack used to blacken the faces of the disks was not considered significant in the calculations. All disks showed less than 3% variation from the average heat input values. Only a very slight "venetian blind effect" was noticed from the spacing of the tungsten lamp filaments. The resultant calibration curve from data from both banks of bulbs is shown in Fig. 9. The outputs of each bank varied by less than 1% when both banks were run together. This variation can be reduced by the proper selection of individual bulbs and the proper adjustment of the bulb spacing and the distances from the bulbs to the blackened copper face.

Equation (3), with either of the three sets of boundary conditions (Figs. 1, 2, or 3), may be solved by a generalized adaptation of the method outlined by Curtis and Ehrlich.^{*} Their program employs the method of Crank

^{*}Curtis, M., and Ehrlich, L., "Multi-material One-dimensional Heat Equation Solver," *STL Programming Handbook for the 704*, February, 1959.

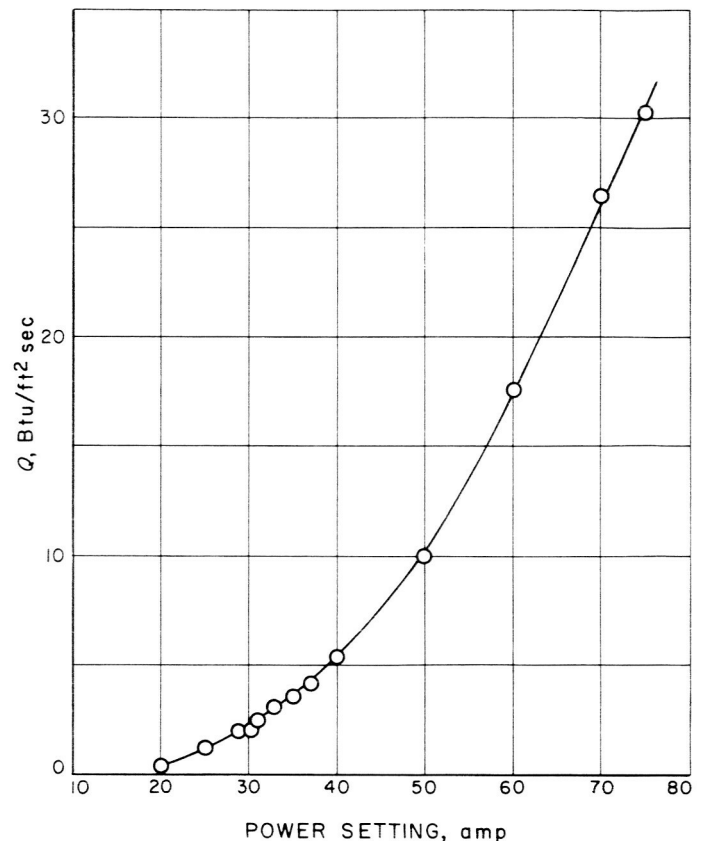


Fig. 9. Calibration curve for radiant heater facility

and Nicolson to yield a tri-diagonal matrix which is in turn solved by Gaussian elimination and backward substitution. This technique predicts the temperature at any time and the position for any given set of thermal properties. Since it is as yet rather difficult to reverse the solution and solve directly for the conductivity, an iteration procedure becomes necessary.

An initial guess of the thermal conductivity and constant density, and a linear approximation of the specific heat (extrapolated from Appendix A) were fed into the computer, and the time-temperature solutions for any single position on the specimen were compared (with the measured data) by a least-squares technique (Appendix B). Using this comparison, the computer selected a new "guess" for the conductivity and repeated the solution cycle. X-Y plots for a solution based on a first guess and for a second solution taken about 10 cycles later are shown in Fig. 10. The scatter in the data points is due to human error in converting recording oscillograph traces into temperatures rather than any real variation in the system.

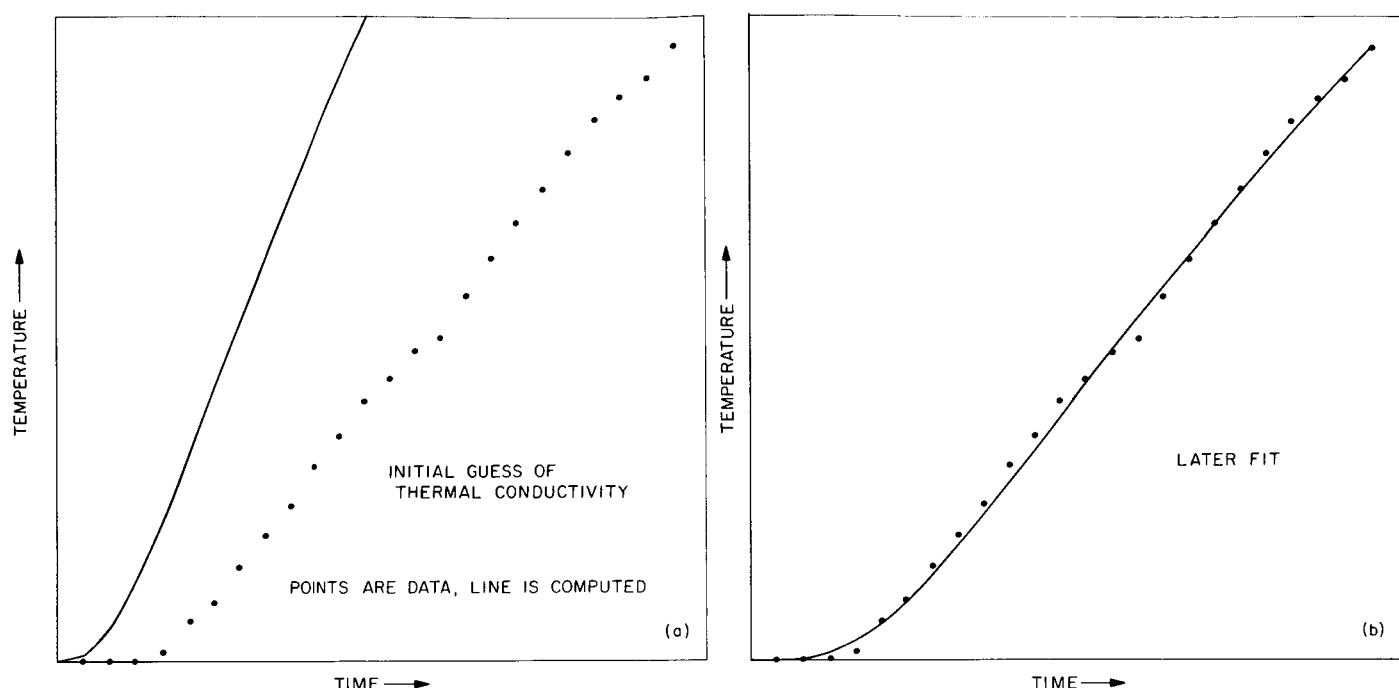


Fig. 10. X-Y trace for constant surface temperature run P1-7 (polyethylene)

III. RESULTS AND DISCUSSION

Preliminary results of the double iteration computer program are listed in Table 1 for three "commercial" polymers (polyethylene, polytetrafluoroethylene and polymethylmethacrylate). Only Model I (using a constant surface temperature) proved feasible with the present apparatus. In Models II and III (using constant heat

fluxes to the copper surface), lateral heat-flow and thermocouple problems limited the value of the experimental data and provided unrealistic conductivity relations. The linear thermal conductivity relations from method I are plotted in Figs. 11, 12, and 13, along with the available literature data on the three polymers. All three polymers

Table 1. Linear thermal conductivities from transient data (Model I), $k = k_0 + bv$; $v = T - T_0$

Polymer	Temperature range, °F	$k_0 \times 10^4$, Btu/ft ² sec °F/ft	$b \times 10^7$, Btu/ft sec	Temperature range, °C	$k_0 \times 10^4$, cal/cm ² sec °C/cm	$b \times 10^7$, cal/cm sec	Run
Polyethylene	64.5 → 218.9	0.294	-0.239	18.1 → 103.8	4.40	-3.56	P 1-6
Polyethylene	64.5 → 361.0	0.301	-0.156	18.1 → 182.8	4.45	-2.32	P 1-7
Polytetrafluoroethylene	64.5 → 263.7	0.227	1.40	18.1 → 128.7	3.38	20.9	T 1-1
Polymethylmethacrylate	66.5 → 155.5	0.264	0.0165	18.6 → 68.6	3.93	0.246	L 1-3
Polymethylmethacrylate	66.5 → 285.8	0.256	0.1613	19.2 → 141.0	3.82	2.40	L 1-4

showed good order of magnitude agreement with the literature values, although both the polyethylene and polytetrafluoroethylene plots were slightly low. None of the computer programs were allowed to run to completion. Examination of the final X-Y plots indicates that further computer time would improve rather than lessen agreement with the literature values. All of the linear curves for thermal conductivity would rise a small but significant amount if the initial 3 to 5 sec delay in obtaining a constant surface temperature was eliminated.

There are three major limiting factors still inherent in using method I to measure the thermal conductivity of homogeneous polymeric materials. The first factor is the temperature limit. Surface contact is lost or lessened at the copper-specimen interface as soon as the polymer "melts" and/or begins evolving gaseous degradation products. The thermoplastics used in this study are, therefore, less adaptable to this method of measuring conductivities than the more dimensionally stable thermosetting plastics. The method may be applicable to chars also, but it is difficult to obtain specimens which are both representative of chars from actual use situations and large enough for testing by this method.

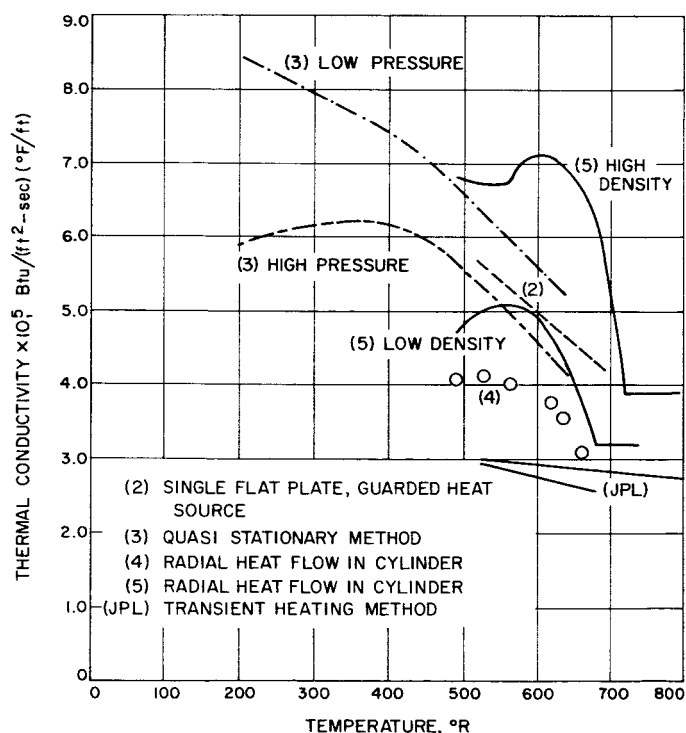


Fig. 11. Thermal conductivity of polyethylene

The second factor concerns the specific heat. Unless detailed knowledge of the variation of specific heat with temperature is known, realistic values for thermal conductivity cannot be calculated by this method. Specific heats should be measured on several samples from the specific lot to be used for thermal conductivity measurements. In this investigation, specific heats were not measured. Instead, linear approximations of specific heat over the temperature range of each run were extrapolated from the available literature data (Appendix A), emphasizing data from specimens judged to be most similar.

The third factor involves the long computer times necessary for convergence of the problem equations. The cost involved for a least-squares fit of the data with a two-constant iteration in the basic equation is prohibitive in comparison with more commonly used steady state techniques for the same temperature range. Higher polynomials could be used to approximate the thermal properties without disrupting the applicability of the present computer program, but such increases in accuracy would only increase the already prohibitive time element to convergence.

It is interesting to note the wide range of thermal conductivity values available in the literature for each polymer (see Figs. 11, 12, and 13). These large variations are easily attributable to differences in density, crystallinity, and internal stressing due to variations in the processing of the different samples. One must, therefore, be careful in using literature data since at any single temperature, changes in processing techniques can vary the thermal conductivity of a particular sample by as much as 40%. Until more comprehensive studies of polymers are available, thermal conductivities should be established experimentally by the user for each new lot used.

Steady state tests were attempted with the radiant heater facility using thinner specimens (approximately 1/32 in.) so that the steady state heat flux could be read on the present equipment. The controller was used to hold the temperature on the hot surface while the cold surface was water cooled to a constant temperature. Specimens run under identical conditions varied widely in their measured thermal conductivities regardless of the care taken in making the specimens identical. A single specimen could be run several times with identical results, but adjacently cut specimens did not agree. Additional thickness is apparently needed to average out the effects of crystallinity, processing, etc.

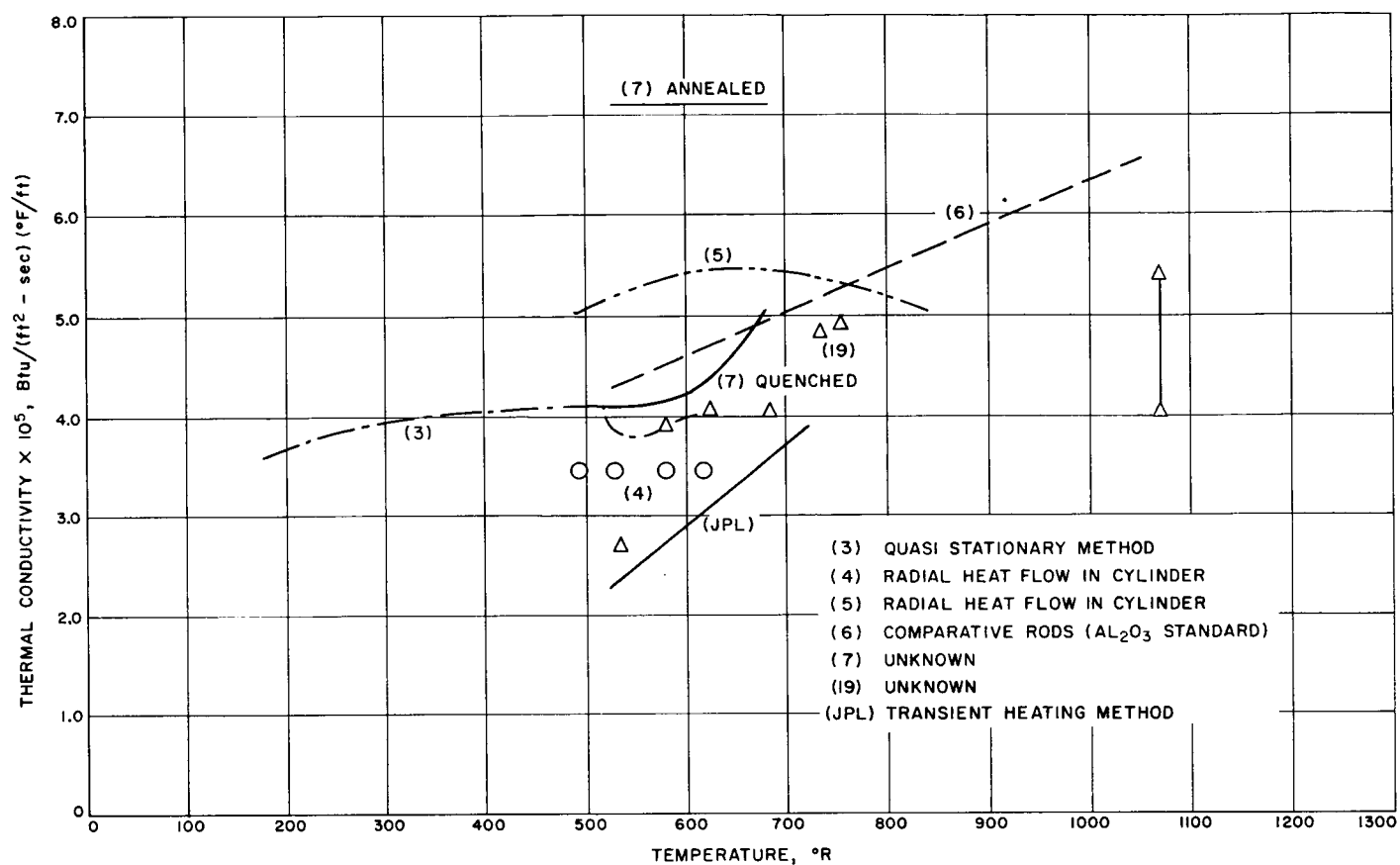


Fig. 12. Thermal conductivity of polytetrafluoroethylene

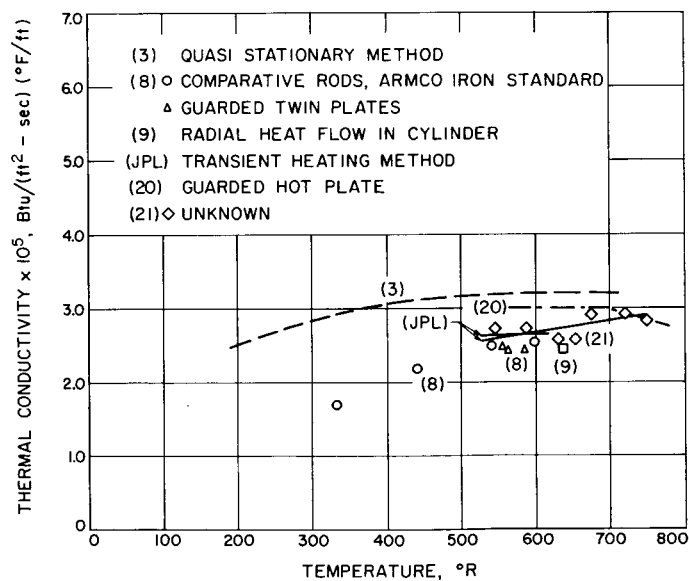


Fig. 13. Thermal conductivity of polymethylmethacrylate

IV. CONCLUSIONS

1. A method of measuring thermal conductivity in homogeneous polymeric materials using transient data has been developed. The method gives linear relationships between thermal conductivity and temperature which are reproducible over any temperature range below the melt temperature of the material investigated.
2. At this time, the method is not considered practical in comparison to other available techniques. This is due to the high cost which accompanies any two-constant iteration procedure.
3. Care must be taken in using literature data since differences in processing techniques may vary the thermal conductivity of a particular polymer by as much as 40%.

ACKNOWLEDGMENTS

The author wishes to thank the many people who aided in the formation of the methods and techniques outlined in this Report. Much of the experimental work was carried out by Thomas Baugh and Thomas Patrick. The computer techniques were adapted by Edgar M. Blizzard. Many helpful changes and variations were taken from discussions with Howard E. Martens and Dr. L. D. Jaffe.

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APPENDIX A

Specific Heat Data for Polyethylene (Fig. A-1),
Polytetrafluoroethylene (Fig. A-2),
and Polymethylmethacrylate (Fig. A-3).

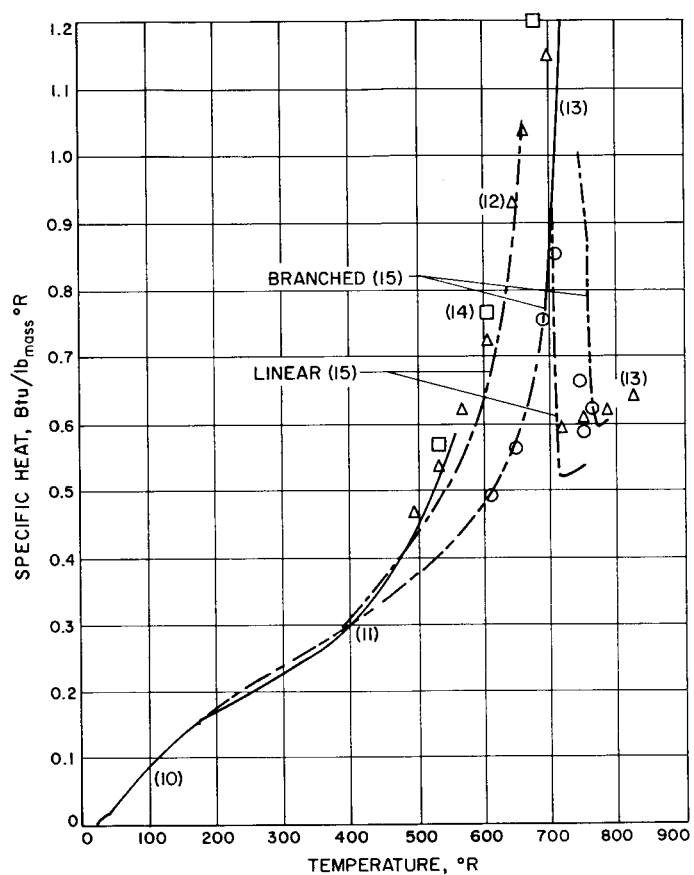


Fig. A-1. Specific heat of polyethylene

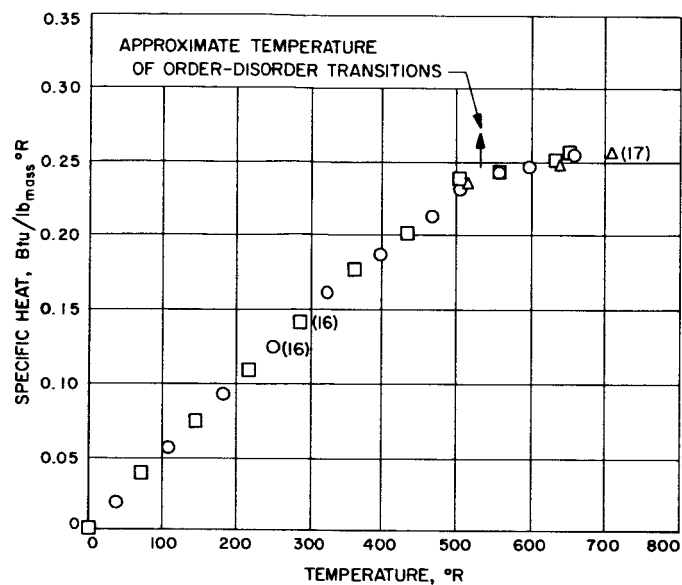


Fig. A-2. Specific heat of polytetrafluoroethylene

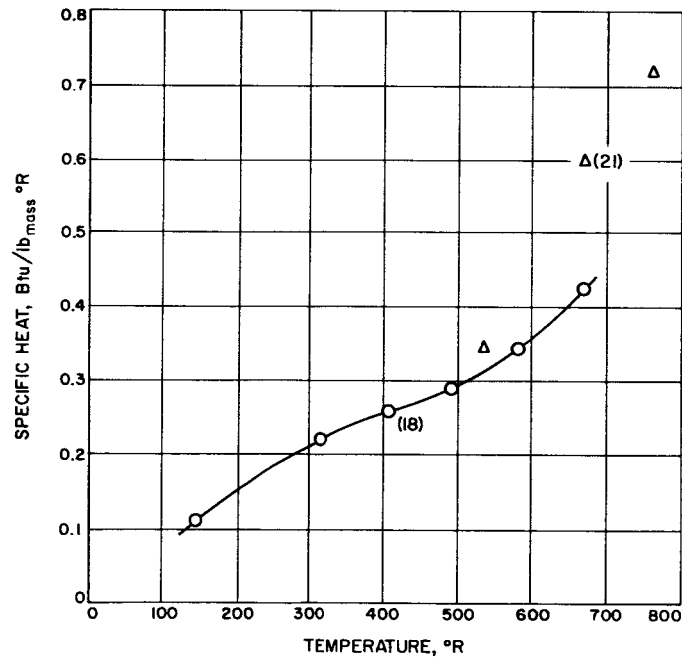


Fig. A-3. Specific heat of polymethylmethacrylate

APPENDIX B

An Outline of the Least-Squares Technique Used in Matching Time-Temperature Curves with Linear Thermal Conductivities

Edgar M. Blizzard and Robert J. Jirka

The form of the one-dimensional heat equation is assumed to be

$$\frac{\partial v}{\partial t} = \frac{1}{\rho C_p(v)} \frac{\partial}{\partial x} \left(k(v) \frac{\partial v}{\partial x} \right) \quad (\text{B-1})$$

where:

v = Relative temperature

t = Time

$k(v) = k_0 + bv$

Given a temperature profile, $\tau_i(t_i)$ vs t_i ($i = 1, \dots, n$), at some point, x_l , $k(v)$ is to be determined in the least-squares sense (n = number of observations).

With the above definition of $k(v)$, Eq. (B-1) becomes

$$\frac{\partial v}{\partial t} = \frac{1}{\rho C_p} \left[b \left(\frac{\partial v}{\partial x} \right)^2 + (k_0 + bv) \frac{\partial^2 v}{\partial x^2} \right] \quad (\text{B-2})$$

The solution of Eq. (B-2) is of the form

$$v = f(x, t, k_0, b) \quad (\text{B-3})$$

At the point $x = x_l$, and at specific times t_i ,

$$v_i = f(x_l, t_i, k_0, b) \quad (\text{B-4})$$

In the least-squares sense the following function must then be minimized:

$$\sum_{i=1}^n [v_i - \tau_i]^2 = E \quad (\text{B-5})$$

Expanding f in Taylors series about (k'_0, b') , using initial guesses for (k_0, b) , and dropping the high order terms

$$f(x_l, t_i, k_0, b) = f(x_l, t_i, k'_0, b') + \frac{\partial f}{\partial k_0} \left[\frac{(k_0 - k'_0)}{k'_0 b'} \right] + \frac{\partial f}{\partial b} \left[\frac{(b - b')}{k'_0 b'} \right] \quad (\text{B-6})$$

Letting $\Delta k_0 = k_0 - k'_0$, $\Delta b = b - b'$ and substituting Eq. (B-6) into Eq. (B-5)

$$\sum_{i=1}^n \left[\tau_i - f(x_l, t_i, k'_0, b') - \frac{\partial f}{\partial k_0} \Delta k_0 - \frac{\partial f}{\partial b} \Delta b \right]^2 = E \quad (\text{B-7})$$

For minimization, k_0 and b must be formed to satisfy

$$[\text{letting } f_i = f(x_l, t_i, k'_0, b')]$$

$$\left. \begin{aligned} \frac{\partial E}{\partial \Delta k_0} &= \sum_{i=1}^n 2 \left[\tau_i - f_i - \frac{\partial f_i}{\partial k_0} \Delta k_0 - \frac{\partial f_i}{\partial b} \Delta b \right] \left(- \frac{\partial f_i}{\partial k_0} \right) = 0 \\ \frac{\partial E}{\partial \Delta b} &= \sum_{i=1}^n 2 \left[\tau_i - f_i - \frac{\partial f_i}{\partial k_0} \Delta k_0 - \frac{\partial f_i}{\partial b} \Delta b \right] \left(- \frac{\partial f_i}{\partial b} \right) = 0 \end{aligned} \right\} \quad (\text{B-8})$$

Rearranging terms,

$$\left. \begin{aligned} \sum_{i=1}^n \left[(\tau_i - f_i) \frac{\partial f_i}{\partial k_0} \right] &= \Delta k_0 \sum_{i=1}^n \left(\frac{\partial f_i}{\partial k_0} \right)^2 + \Delta b \sum_{i=1}^n \left(\frac{\partial f_i}{\partial k_0} \right) \left(\frac{\partial f_i}{\partial b} \right) \\ \sum_{i=1}^n \left[(\tau_i - f_i) \frac{\partial f_i}{\partial b} \right] &= \Delta a \sum_{i=1}^n \left(\frac{\partial f_i}{\partial k_0} \right) \left(\frac{\partial f_i}{\partial b} \right) + \Delta b \sum_{i=1}^n \left(\frac{\partial f_i}{\partial b} \right)^2 \end{aligned} \right\} \quad (\text{B-9})$$

Setting $\psi_i = \frac{\partial f_i}{\partial k_0}$ and $\psi'_i = \frac{\partial f_i}{\partial b}$,

Then

$$\begin{aligned} \frac{\partial \psi_i}{\partial t_i} &= \frac{\partial}{\partial t} \left(\frac{\partial f_i}{\partial k_0} \right) = \frac{\partial}{\partial k_0} \left(\frac{\partial f_i}{\partial t_i} \right) = \frac{\partial}{\partial k_0} \left(\frac{\partial v_i}{\partial t} \right) \\ &= \frac{1}{(\rho C_p)_i} \frac{\partial^2 v_i}{\partial x^2} \quad \text{where } \bar{\psi}_i(k_0, 0) = 0 \end{aligned} \quad (\text{B-10})$$

In like manner,

$$\frac{\partial \psi'_i}{\partial t_i} = \frac{1}{(\rho C_p)_i} \left[\left(\frac{\partial v_i}{\partial x} \right)^2 + v_i \frac{\partial^2 v_i}{\partial x^2} \right] \quad \text{where } \psi'_i(b, 0) = 0 \quad (\text{B-11})$$

The computational sequence is:

1. Select initial guesses: $k = k_0, b = b_0$
2. Solve to $t = t_i, i = 1, 2, \dots, n$

$$\left. \begin{aligned} \text{a. } \frac{\partial v}{\partial t} &= \frac{1}{\rho C_p} \left[b \left(\frac{\partial v}{\partial x} \right)^2 + (k_0 + bv) \frac{\partial^2 v}{\partial x^2} \right] \\ \text{b. } \frac{\partial \psi}{\partial t} &= \frac{1}{\rho C_p} \frac{\partial^2 v}{\partial x^2} \\ \text{c. } \frac{\partial \psi'}{\partial t} &= \frac{1}{\rho C_p} \left[\left(\frac{\partial v}{\partial x} \right)^2 + v \frac{\partial^2 v}{\partial x^2} \right] \end{aligned} \right\} \begin{array}{l} \text{Solve using C-N} \\ \text{heat equation} \\ \text{solver} \\ \\ \text{Solve using} \\ \text{finite differences} \end{array}$$

3. At the point $x = x_i$ form

$$\sum_{i=1}^n (\tau_i - v_i) \psi_i, \sum_{i=1}^n \psi_i \cdot \psi'_i, \sum_{i=1}^n (\tau_i - v_i) \psi'_i, \sum \psi_i^2, \sum (\psi'_i)^2$$

4. Solve Eq. (B-9) for Δk_0 and Δb

5. Set $k_{0_i} = k_{0_{i-1}} + \Delta k_0$

$$b_i = b_{i-1} + \Delta b$$

6. $|\Delta k_0| < \varepsilon_1, |\Delta b| < \varepsilon_2$

7. Yes \rightarrow Stop, No \rightarrow Go to Step 2